

Transport Coefficients of van der Waals Fluids and Fluid Mixtures

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We propose models which are direct extensions to dynamical domains of van Kampen's approach to van der Waals fluids, and are suited for studying transport phenomena near critical points. Models are described by hydrodynamic equation for hard sphere fluids where long range interactions are added as semi-macroscopic forces acting among mass elements of the fluids, and are in principle capable of rigorous treatment of critical anomalies. Here we used the models to obtain the lowest order corrections of critical fluctuations to transport coefficients. Denoting the force range by l and the reduced temperature distance from the critical point by ϵ , we found the following lowest order corrections: (a) for one-component fluids, shear viscosity $\eta \sim l^{-1}|\epsilon|^{-1/2}$, bulk viscosity $\zeta \sim l^{-1}|\epsilon|^{-5/2}$, thermal conductivity $\lambda \sim l^{-1}|\epsilon|^{-1/2}$, and (b) for binary solutions near critical solution points, diffusion constant $D \sim l^{-1}|\epsilon|^{1/2}$, $\eta \sim \text{constant} + l^{-1}|\epsilon|^{1/2}$, $\zeta \sim l^{-1}|\epsilon|^{-3/2}$, $\lambda \sim l^{-1}|\epsilon|^{-1/2}$, and thermal diffusion constant $D^T \sim l^{-1}|\epsilon|^{-1/2}$.

§ 1. Introduction

In recent years we have seen substantial progress towards our understanding of anomalous transport phenomena near the critical point.¹⁾ Among others, extensions of the Widom-Kadanoff scaling law idea to dynamical domains²⁾ have been particularly fruitful. There have been some attempts to examine this dynamical scaling hypothesis on the basis of the mode-mode coupling approach to transport coefficients^{1),3)} and its generalizations.^{4),5)} We have been able to show that in some cases dynamics of critical fluctuations is governed by equal-time correlations of certain long wave length fluctuations where the dynamical scaling holds, and in some other cases rapid random motions associated with short wave length fluctuations affect the dynamics of critical fluctuations where the dynamical scaling does not necessarily holds.⁴⁾ Our understanding of the latter cases is far from being satisfactory although some useful relations among transport coefficients have been obtained,³⁾ and puzzling experimental results are appearing.¹⁾

A purpose of the present paper is to propose models which will be useful in the study of anomalous transport phenomena where the dynamical scaling does not work. In particular, we consider liquid-gas transition in one-component fluids and demixing of binary solutions. Our models are essentially van der Waals fluids. The van der Waals fluids have been used previously for similar purposes. Zwanzig and the coworkers⁶⁾ developed a mode-mode coupling approach to transport coefficients of the model van der Waals fluids of van Kampen.⁷⁾ Their approach, however, is more phenomenological than what is required in the model

of van Kampen. De Sobrino⁸⁾ recently treated a hard sphere gas interacting with long range attractive forces, and obtained anomalous transport coefficients near the critical point. His treatment appears to be rather complicated, and it is not easy to assess his results in view of various approximations introduced.

In the present paper we adopt a viewpoint similar to those of the above-mentioned authors. We generalize van Kampen's treatment of van der Waals fluids to dynamical domains, however, with less phenomenological assumptions than Zwanzig and the coworkers, and propose precise models (§ 2). Then we consider anomalous transport coefficients for these models (§ 4), thereby avoiding the complications of de Sobrino's treatment.

§ 2. Van der Waals fluids

a. One-component fluids

We consider an assembly of N particles of mass m whose inter-particle potential consists of a hard sphere interaction of range σ and an attractive part $-w(\mathbf{r})$ with the force range l which is assumed to be very large compared to σ : $l \gg \sigma$. Near the critical point where the number density of particles is nearly $1/2\pi\sigma^3$,⁸⁾ we have three lengths characterizing the problem: σ , l , and the correlation range of critical fluctuations ξ where obviously $\xi \gtrsim l$.*) Thus, as long as we are concerned with phenomena occurring over the distances which are sufficiently large compared to σ but are small compared to l , and over the time intervals which are sufficiently long compared to the microscopic time $\sigma/\sqrt{k_B T/m}$ of the hard sphere fluid but are short compared to $l/\sqrt{k_B T/m}$, the dynamical behavior of the system is well described by the following hydrodynamic equations of a hard sphere fluid in which the long-ranged potential $-w(\mathbf{r})$ is added as a force acting among mass elements of the fluid, which in fact is a direct extension to non-equilibrium domain of van Kampen's treatment of equilibrium phenomena:⁷⁾

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (2 \cdot 1a)$$

$$\begin{aligned} \rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = & - \nabla p_h + \frac{\partial}{\partial r_j} \left\{ \eta_h \left(\frac{\partial \mathbf{v}}{\partial r_j} + \nabla v_j \right) \right\} \\ & + \nabla \left\{ \left(\zeta_h - \frac{2}{3} \eta_h \right) \nabla \cdot \mathbf{v} \right\} + \rho(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \int \frac{w(\mathbf{r}-\mathbf{r}')}{m^2} \rho(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (2 \cdot 1b)$$

$$\begin{aligned} \rho T \left(\frac{\partial S_h}{\partial t} + \mathbf{v} \cdot \nabla S_h \right) = & \nabla \cdot (\lambda_h \nabla T) + \eta_h \frac{\partial v_i}{\partial r_j} \left(\frac{\partial v_i}{\partial r_j} + \frac{\partial v_j}{\partial r_i} \right) \\ & + \left(\zeta_h - \frac{2}{3} \eta_h \right) (\nabla \cdot \mathbf{v})^2 + \rho(\mathbf{r}) \mathbf{v}(\mathbf{r}) \cdot \frac{\partial}{\partial \mathbf{r}} \int \frac{w(\mathbf{r}-\mathbf{r}')}{m^2} \rho(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (2 \cdot 1c)$$

*) Since we do not consider non-local transport properties in this paper, the length characterizing spatial inhomogeneity of the macroscopic state is left out.

where we have used the following notations: ρ -local mass density, \mathbf{v} -local velocity, p_h -local pressure, S_h -local entropy per unit mass, η_h -local shear viscosity, ζ_h -local bulk viscosity, λ_h -local thermal conductivity, k_B -the Boltzmann constant, and T -absolute temperature. The subscripts h imply that these quantities refer to the hard sphere fluid, and the Einstein convention has been used for the summations over the indices $i, j = x, y, z$.

The hydrodynamic equations (2.1) are themselves approximate equations to describe the time evolution of the system. Nevertheless, by choosing the ratio l/σ arbitrarily large we can make (2.1) precise over arbitrarily large regions of space and time. Thus hereafter we shall regard (2.1) as a semi-macroscopic model of our van der Waals fluid, and study its transport properties. It is reasonable to expect that, if necessary, the model can be justified for the system under consideration. In this sense our approach differs from earlier more phenomenological approaches.^{1),6),9)}

Although Eqs. (2.1) are valid even if the hard sphere potential is replaced by other short-range repulsive potentials after suitably redefining quantities with subscripts h , the present choice of hard sphere potential brings in certain simplifications. Also, as is well known, $w(\mathbf{r})$ must satisfy the condition that

$$w_0 \equiv \int w(\mathbf{r}) d\mathbf{r} \quad (2.2)$$

remains finite for arbitrarily large l in order to obtain a sensible van der Waals limit. For instance, we may take the following Yukawa type potential:

$$w(\mathbf{r}) = \frac{w_0}{4\pi l^2} \frac{e^{-r/l}}{r}. \quad (2.3)$$

We further note that our model includes the case $\xi \gg l$, and thus, in principle, is capable of dealing with the truly asymptotic critical region.

Let us rewrite Eqs. (2.1) by taking ρ , T and \mathbf{v} as independent variables. For hard sphere fluids pressure and entropy have the following forms:

$$p_h = k_B T \Pi(\rho), \quad (2.4)$$

$$S_h = S_f(\rho) + \frac{3k_B}{2m} \ln T, \quad (2.5)$$

where $\Pi(\rho)$ is some function of ρ and $S_f(\rho)$ is the configurational contribution to the entropy and $3k_B \ln T/2m$ comes from kinetic energy. Use of Maxwell's relation $(\partial p_h / \partial T)_\rho = -\rho^2 (\partial S_h / \partial \rho)_T$ yields

$$k_B \Pi(\rho) = -\rho^2 dS_f(\rho) / d\rho. \quad (2.6)$$

Then in (2.1b) we have

$$\nabla p_h = k_B \Pi(\rho) \nabla T + k_B T \Pi'(\rho) \nabla \rho \quad (2.6')$$

and the l. h. s. of (2.1c) becomes, using the continuity equation (2.1a),

$$\rho T \left(\frac{\partial S_h}{\partial t} + \mathbf{v} \cdot \nabla S_h \right) = \frac{3k_B}{2m} \rho \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) - \rho^2 T S_f'(\rho) \nabla \cdot \mathbf{v}, \quad (2.7)$$

where primes indicate derivatives with respect to ρ . Since λ_h, η_h and ζ_h are definite functions of ρ and T , we obtain a closed set of equations describing the time evolution of ρ, \mathbf{v} and T .

b. Binary solutions

The system considered is similar to the one considered by Deutch and Zwanzig,⁹⁾ namely an assembly of N_A particles of the species A and N_B particles of the species B with the same mass m , where the inter-particle interactions have, besides the common hard sphere interaction of range σ , long-ranged attractive parts which depend on the kinds of interacting particles and are denoted by $-w_{AA}(\mathbf{r}), -w_{AB}(\mathbf{r})$, and $-w_{BB}(\mathbf{r})$ in obvious notation. The semi-macroscopic hydrodynamic equations that correspond to (2.1) then read

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (2.8a)$$

$$\rho \left(\frac{\partial \mathbf{c}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{c} \right) = -\nabla \cdot \mathbf{i}, \quad (2.8b)$$

$$\begin{aligned} \rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) &= -\nabla p_h + \frac{\partial}{\partial r_j} \left\{ \eta_h \left(\frac{\partial \mathbf{v}}{\partial r_j} + \nabla v_j \right) \right\} + \nabla \cdot \left\{ \left(\zeta_h - \frac{2}{3} \eta_h \right) \nabla \cdot \mathbf{v} \right\} \\ &+ \frac{1}{m^2} \rho(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \int [w_{BA}(\mathbf{r}-\mathbf{r}')c(\mathbf{r}') + w_{BB}(\mathbf{r}-\mathbf{r}') (1-c(\mathbf{r}'))] \rho(\mathbf{r}') d\mathbf{r}' \\ &+ \frac{1}{m^2} \rho(\mathbf{r}) c(\mathbf{r}) \frac{\partial}{\partial \mathbf{r}} \int [w_{AB}(\mathbf{r}-\mathbf{r}') - w_{BB}(\mathbf{r}-\mathbf{r}') + 2w(\mathbf{r}-\mathbf{r}')c(\mathbf{r}')] \rho(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (2.8c)$$

$$\begin{aligned} \rho T \left(\frac{\partial S_h}{\partial t} + \mathbf{v} \cdot \nabla S_h \right) &= \eta_h \frac{\partial v_i}{\partial r_j} \left(\frac{\partial v_i}{\partial r_j} + \frac{\partial v_j}{\partial r_i} \right) + \left(\zeta_h - \frac{2}{3} \eta_h \right) (\nabla \cdot \mathbf{v})^2 \\ &+ \nabla \cdot \left(\lambda_h \nabla T - \frac{\beta_h T}{\alpha_h} \mathbf{i} \right) - \mathbf{i} \cdot \nabla \mu_h + \frac{1}{m^2} \rho(\mathbf{r}) \mathbf{v}(\mathbf{r}) \cdot \frac{\partial}{\partial \mathbf{r}} \int [w_{BA}(\mathbf{r}-\mathbf{r}')c(\mathbf{r}') \\ &+ w_{BB}(\mathbf{r}-\mathbf{r}') (1-c(\mathbf{r}'))] \rho(\mathbf{r}') d\mathbf{r}' + \frac{1}{m^2} [\rho(\mathbf{r})c(\mathbf{r})\mathbf{v}(\mathbf{r}') + \mathbf{i}(\mathbf{r})] \\ &\times \frac{\partial}{\partial \mathbf{r}} \int [w_{AB}(\mathbf{r}-\mathbf{r}') - w_{BB}(\mathbf{r}-\mathbf{r}') + 2w(\mathbf{r}-\mathbf{r}')c(\mathbf{r}')] \rho(\mathbf{r}') d\mathbf{r}', \end{aligned} \quad (2.8d)$$

$$\mathbf{i} = -\alpha_h \nabla \mu_h - \beta_h \nabla T, \quad (2.8e)$$

where, writing ρ_A, ρ_B and $\mathbf{v}_A, \mathbf{v}_B$ for the mass densities and velocities of components A and B respectively,

$$\rho = \rho_A + \rho_B, \quad (\text{total mass density}) \quad (2.9a)$$

$$c = \rho_A / \rho, \quad (\text{relative concentration}) \quad (2.9b)$$

$$\mathbf{v} = c\mathbf{v}_A + (1-c)\mathbf{v}_B, \quad (\text{average velocity}) \quad (2.9c)$$

$$\mathbf{i} = \rho c(1-c)(\mathbf{v}_A - \mathbf{v}_B), \quad (\text{diffusion current}) \quad (2.9d)$$

$$\tau\omega(\mathbf{r}) \equiv \frac{1}{2}[\tau\omega_{AA}(\mathbf{r}) + \tau\omega_{BB}(\mathbf{r}) - 2\tau\omega_{AB}(\mathbf{r})]. \quad (2.9e)$$

$\mu_h(p_h, c, T)$ is the chemical potential, and α_h and β_h are the kinetic coefficients related to the diffusion constant D_h and the thermal diffusion ratio k_h^T by

$$\left. \begin{aligned} D_h &= \frac{\alpha_h}{\rho} \left(\frac{\partial \mu_h}{\partial c} \right)_{T, p_h}, \\ \rho k_h^T D_h / T &= \alpha_h (\partial \mu_h / \partial T)_{c, p_h} + \beta_h. \end{aligned} \right\} \quad (2.10)^*$$

The subscripts h refer to hard sphere fluids as before.

In the van der Waals limit it is readily seen that the extra Helmholtz free energy ΔF which depends upon the concentration c and involves attractive forces is written as

$$\begin{aligned} \Delta F &= Nk_B T [c \ln c + (1-c) \ln c] \\ &\quad - \frac{V}{2m^2} \rho^2 [\tau\omega_0^{AA} c^2 + \tau\omega_0^{BB} (1-c)^2 + 2\tau\omega_0^{AB} c(1-c)], \end{aligned} \quad (2.11)$$

where $N = N_A + N_B$ and

$$\tau\omega_k^{AB} = \int \tau\omega_{AB}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}, \quad \text{etc.} \quad (2.12)$$

The first term of (2.11) is the extra free energy of the hard sphere fluid mixture.

The chemical potential μ is obtained from (2.11) and is

$$\mu = \left[\frac{\partial (\Delta F / Nm)}{\partial c} \right]_{\rho, T} = \mu_h - \frac{\rho}{m^2} (\tau\omega_0^{AB} - \tau\omega_0^{BB} + 2c\tau\omega_0), \quad (2.13)$$

where μ_h is the chemical potential of the hard sphere fluid mixture given by

$$\mu_h = \frac{k_B T}{m} \ln \frac{c}{1-c}. \quad (2.14)$$

The pressure is also obtained from (2.11) and is

$$p = p_h - \frac{\rho^2}{2m^2} [\tau\omega_0^{AA} c^2 + \tau\omega_0^{BB} (1-c)^2 + 2\tau\omega_0^{AB} c(1-c)], \quad (2.15)$$

where p_h is the same as that for one component fluid given by (2.4) and thus does not depend on c .

The entropy is found from the formula $S = -[\partial (F/Nm) / \partial T]_{\rho, c}$, and is

$$\begin{aligned} S &= S_f(\rho) + \frac{3k_B}{2m} \ln T - \frac{k_B}{m} [c \ln c + (1-c) \ln(1-c)] \\ &= S_h. \end{aligned} \quad (2.16)$$

*) See L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, 1959), Chapter VI.

§ 3. Equations of motion near the critical point

a. One-component fluids

Equations (2.1) can be put into the following form with the use of (2.6') and (2.7), and separating out the terms linear in the deviations from equilibrium to the l. h. s.;

$$\frac{\partial \rho_1}{\partial t} + \rho_0 \nabla \cdot \mathbf{v} = K_0, \tag{3.1a}$$

$$\begin{aligned} \frac{\partial \mathbf{v}}{\partial t} + \frac{k_B}{\rho_0} (\Pi_0 \nabla T + T_0 \Pi_0' \nabla \rho) - \frac{\eta_{h0}}{\rho_0} \nabla^2 \mathbf{v} \\ - \frac{1}{\rho_0} \left(\zeta_{h0} + \frac{1}{3} \eta_{h0} \right) \nabla (\nabla \cdot \mathbf{v}) - \frac{\partial}{\partial \mathbf{r}} \int \frac{\omega(\mathbf{r} - \mathbf{r}')}{m^2} \rho_1(\mathbf{r}') d\mathbf{r}' = \mathbf{K}, \end{aligned} \tag{3.1b}$$

$$\frac{3k_B}{2m} \frac{\partial T_1}{\partial t} - \rho_0 T_0 S_{T0}' \nabla \cdot \mathbf{v} - \frac{\lambda_{h0}}{\rho_0} \nabla^2 T_1 = K_1, \tag{3.1c}$$

where subscripts 0 and 1 refer to equilibrium values and derivations from them, respectively, and K_0 , \mathbf{K} and K_1 are non-linear in these deviations.

Since we shall use a linearized set of hydrodynamical equations of (3.1) in § 4, we consider its properties near the critical point in the van der Waals limit $l \rightarrow \infty$. If we introduce Fourier transforms by

$$\rho_{\mathbf{k}} = \int \rho_1(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}), \text{ etc.},$$

we find for (3.1b) with $\mathbf{K} = 0$, using (2.4),

$$\begin{aligned} \frac{\partial \mathbf{v}_{\mathbf{k}}}{\partial t} - i\mathbf{k} \frac{1}{\rho_0} \left(\frac{\partial p_h}{\partial T} \right)_{T_0} T_{\mathbf{k}} - i\mathbf{k} \left[\frac{1}{\rho_0} \left(\frac{\partial p_h}{\partial \rho} \right)_{T_0} - \frac{1}{m^2} \omega_{\mathbf{k}} \right] \rho_{\mathbf{k}} \\ + \frac{\eta_{h0}}{\rho_0} k^2 \mathbf{v}_{\mathbf{k}} + \frac{1}{\rho_0} \left(\zeta_{h0} + \frac{1}{3} \eta_{h0} \right) \mathbf{k} (\mathbf{k} \cdot \mathbf{v}_{\mathbf{k}}) = 0. \end{aligned} \tag{3.2}$$

In the van der Waals limit the pressure p is given by

$$p = p_h - \frac{\rho^2}{2m^2} \omega_0. \tag{3.3}$$

Thus the quantity in the square bracket of (3.2) is written as

$$\frac{1}{\rho_0} \left(\frac{\partial p}{\partial \rho} \right)_{T_0} + \nu_{\mathbf{k}} \tag{3.4}$$

with

$$\nu_{\mathbf{k}} \equiv \frac{1}{m^2} (\omega_0 - \omega_{\mathbf{k}}).$$

We also have

$$(\partial p_h / \partial T)_{V_0} = (\partial p / \partial T)_{V_0}. \quad (3.5)$$

By the use of Maxwell's relation one can easily demonstrate that entropy in the van der Waals limit is identical to S_h . Thus the specific heat at constant volume is $C_V = 3k_B/2m$.

We thus obtain the linearized hydrodynamic equations for very large l ,

$$\frac{\partial \rho_{\mathbf{k}}}{\partial t} - \rho_0 i \mathbf{k} \cdot \mathbf{v}_{\mathbf{k}} = 0, \quad (3.6a)$$

$$\begin{aligned} \frac{\partial \mathbf{v}_{\mathbf{k}}}{\partial t} - i \mathbf{k} \frac{1}{\rho_0} \left(\frac{\partial p}{\partial T} \right)_{V_0} T_{\mathbf{k}} - i \mathbf{k} \left[\frac{1}{\rho_0} \left(\frac{\partial p}{\partial \rho} \right)_{T_0} + \nu_{\mathbf{k}} \right] \rho_{\mathbf{k}} \\ + \frac{\eta_{h0}}{\rho_0} k^2 \mathbf{v}_{\mathbf{k}} + \frac{1}{\rho_0} \left(\zeta_{h0} + \frac{1}{3} \eta_{h0} \right) \mathbf{k} (\mathbf{k} \cdot \mathbf{v}_{\mathbf{k}}) = 0, \end{aligned} \quad (3.6b)$$

$$C_{V_0} \frac{\partial T_{\mathbf{k}}}{\partial t} + \rho_0 T_0 \left(\frac{\partial S}{\partial \rho} \right)_{T_0} i \mathbf{k} \cdot \mathbf{v}_{\mathbf{k}} + \frac{\lambda_{h0}}{\rho_0} k^2 T_{\mathbf{k}} = 0. \quad (3.6c)$$

The effects of $w(\mathbf{r})$ in (3.6) appear in two places: $w(\mathbf{r})$ affects $(\partial p / \partial \rho)_{T_0}$ and add a term $\nu_{\mathbf{k}}$ in (3.6b). The only anomalous quantity in (3.6) is the inverse isothermal compressibility $\rho_0 (\partial p / \partial \rho)_{T_0}$ which vanishes at the critical point. The van der Waals critical point (ρ_c, T_c) is given implicitly as a solution of the equation^{*}

$$(\partial p_c / \partial \rho_c)_{T_c} = k_B T_c \Pi'(\rho_c) - \frac{\rho_c}{m^2} w_0 = 0 \quad (3.7)$$

and

$$(\partial^2 p_c / \partial \rho_c^2)_{T_c} = k_B T_c \Pi''(\rho_c) - \frac{w_0}{m^2} = 0.$$

In particular, ρ_c is determined by^{*}

$$\Pi'(\rho_c) = \rho_c \Pi''(\rho_c). \quad (3.8)$$

The time evolution of (3.6) is best described by introducing the Laplace transforms of the variables,^{10,11)}

$$\hat{\rho}_{\mathbf{k}}(s) \equiv \int_0^{\infty} dt e^{-st} \rho_{\mathbf{k}}(t), \text{ etc.} \quad (3.9)$$

Laplace transforming (3.6) then yields the following relationships connecting $\hat{\rho}_{\mathbf{k}}(s)$, $\hat{\mathbf{v}}_{\mathbf{k}}(s)$ and $\hat{T}_{\mathbf{k}}(s)$ with the initial values $\rho_{\mathbf{k}}(0)$, $\mathbf{v}_{\mathbf{k}}(0)$ and $T_{\mathbf{k}}(0)$:

^{*}) Van Kampen⁷⁾ chooses $\Pi(\rho) = \rho / (m - \rho \delta)$ where δ is four times the hard sphere volume, and then we have

$$\rho_c = m / 3\delta$$

and

$$T_c = 4w_0 / 27k_B \delta.$$

$$\hat{\rho}_{\mathbf{k}}(s) = \frac{1}{D(\mathbf{k}, s)} \left\{ \left[(s + k^2\theta) \left(s + \frac{\lambda_h}{\rho C_V} k^2 \right) - k^2 \frac{T(\partial p/\partial T)_\rho (\partial S/\partial \rho)_T}{C_V} \right] \rho_{\mathbf{k}}(0) + ik\rho \left(s + \frac{\lambda_h}{\rho C_V} k^2 \right) v_{\mathbf{k}}^L(0) - k^2 \left(\frac{\partial p}{\partial T} \right)_\rho T_{\mathbf{k}}(0) \right\}, \quad (3.10a)$$

$$\hat{v}_{\mathbf{k}}^L(s) = \frac{1}{D(\mathbf{k}, s)} \left\{ ik \left[\frac{1}{\rho} \left(\frac{\partial p}{\partial \rho} \right)_T + \nu_{\mathbf{k}} \right] \left(s + \frac{\lambda_h}{\rho C_V} k^2 \right) \rho_{\mathbf{k}}(0) + s \left(s + \frac{\lambda_h}{\rho C_V} k^2 \right) v_{\mathbf{k}}^L(0) + ik \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho s T_{\mathbf{k}}(0) \right\}, \quad (3.10b)$$

and we have omitted subscripts 0 to denote equilibrium values.

$$\hat{T}_{\mathbf{k}}(s) = \frac{1}{D(\mathbf{k}, s)} \left\{ k^2 \frac{T}{C_V} \left(\frac{\partial S}{\partial \rho} \right)_T \left[\left(\frac{\partial p}{\partial \rho} \right)_T + \rho \nu_{\mathbf{k}} \right] \rho_{\mathbf{k}}(0) - iks \frac{\rho T}{C_V} \left(\frac{\partial S}{\partial \rho} \right)_T v_{\mathbf{k}}^L(0) + \left[s(s + k^2\theta) + k^2 \left(\left(\frac{\partial p}{\partial \rho} \right)_T + \rho \nu_{\mathbf{k}} \right) \right] T_{\mathbf{k}}(0) \right\}, \quad (3.10c)$$

$$\hat{v}_{\mathbf{k}}^T(s) = \frac{v_{\mathbf{k}}^T(0)}{s + (\eta_h/\rho) k^2}, \quad (3.10d)$$

where

$$D(\mathbf{k}, s) \equiv s^3 + \left(\frac{\lambda_h}{\rho C_V} + \theta \right) k^2 s^2 + \left[\left(\left(\frac{\partial p}{\partial \rho} \right)_s + \rho \nu_{\mathbf{k}} \right) k^2 + \frac{\lambda_h \theta}{\rho C_V} k^4 \right] s + \left(\left(\frac{\partial p}{\partial \rho} \right)_T + \rho \nu_{\mathbf{k}} \right) \frac{\lambda_h}{\rho C_V} k^4, \quad (3.10e)^*$$

$$\theta \equiv \left(\frac{4}{3} \eta_h + \zeta_h \right) / \rho, \quad (3.10f)$$

and $v_{\mathbf{k}}^L$ and $v_{\mathbf{k}}^T$ denote longitudinal and transverse components of velocity, respectively, and we have used that

$$\left(\frac{\partial p}{\partial \rho} \right)_s = \left(\frac{\partial p}{\partial \rho} \right)_T - T \left(\frac{\partial p}{\partial T} \right)_\rho \left(\frac{\partial S}{\partial \rho} \right)_T / C_V. \quad (3.11)$$

$D(\mathbf{k}, s)$ can be rewritten as

$$D(\mathbf{k}, s) = s^3 + (a + \theta) k^2 s^2 + (u_{\mathbf{k}}^2 k^2 + a\theta k^4) s + a u_{\mathbf{k}}^2 k^4 / \gamma_{\mathbf{k}} \quad (3.12)^*$$

with

$$\left. \begin{aligned} a &\equiv \lambda_h / \rho C_V, \\ u_{\mathbf{k}} &\equiv \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_s + \rho \nu_{\mathbf{k}}}, \\ \gamma_{\mathbf{k}} &\equiv \left[\left(\frac{\partial p}{\partial \rho} \right)_s + \rho \nu_{\mathbf{k}} \right] / \left[\left(\frac{\partial p}{\partial \rho} \right)_T + \rho \nu_{\mathbf{k}} \right]. \end{aligned} \right\} \quad (3.13)$$

*) For very small k this corresponds to the l.h.s. of Eq. (1.5) of Mountain, reference 11), if we note that $\theta = b$, $u_{\mathbf{k}} \rightarrow C_0$ and $\gamma_{\mathbf{k}} \rightarrow \gamma$ in his notation.

For $k=0$ where $\nu_k=0$, u_k and γ_k reduce to the adiabatic sound speed and to C_p/C_V , respectively, C_p being the specific heat with constant pressure. Then, as in reference 11), for small k the equation $D(\mathbf{k}, s)=0$ has three solutions $s_{\mathbf{k}}^+$, $s_{\mathbf{k}}^-$ and $s_{\mathbf{k}}^0$,

$$D(\mathbf{k}, s) = (s - s_{\mathbf{k}}^+) (s - s_{\mathbf{k}}^-) (s - s_{\mathbf{k}}^0) \quad (3.14)$$

with

$$s_{\mathbf{k}}^{\pm} = \pm i u_k k - \frac{1}{2} \left[\theta + \frac{\lambda_k}{\rho C_V} \left(1 - \frac{1}{\gamma_k} \right) \right] k^2, \quad (3.15a)$$

$$s_{\mathbf{k}}^0 = -\lambda_k k^2 / (\rho C_V \gamma_k). \quad (3.15b)$$

Even for small k we have kept k in γ_k and u_k which arises from ν_k because due to large l these quantities depend sensitively on k even for small $k \gtrsim 1/l$. In fact, for the choice of $w(\mathbf{r})$ given by (2.3) we have $w_{\mathbf{k}} = w_0 / (1 + k^2 l^2)$ and $\nu_{\mathbf{k}} = (w_0/m^2) l^2 k^2 / (1 + l^2 k^2)$, and thus we obtain

$$u_{\mathbf{k}}^2 = u_0^2 \left[1 + \left(1 + \frac{\rho w_0}{m^2 u_0^2} \right) l^2 k^2 \right] / (1 + l^2 k^2), \quad (3.16)$$

$$\gamma_{\mathbf{k}} = \frac{u_0^2 m^2}{w_0 l^2 \rho} \left[1 + \left(1 + \frac{\rho w_0}{m^2 u_0^2} \right) l^2 k^2 \right] \xi^2 / [1 + (l^2 + \xi^2) k^2] \quad (3.17)$$

with

$$\xi^{-2} \equiv (\partial p / \partial \rho)_T \left(\frac{l^2 w_0 \rho}{m^2} \right), \quad (3.18)$$

where ξ is the correlation range of critical fluctuations. For $lk \ll 1$, (3.17) becomes

$$\gamma_{\mathbf{k}} \approx \frac{u_0^2 m^2}{w_0 l^2 \rho} \frac{1}{k^2 + \xi^{-2}}. \quad (3.19)$$

Incidentally we also have⁷⁾

$$\langle |\rho_{\mathbf{k}}|^2 \rangle = \frac{k_B T V \rho}{(\partial p / \partial \rho)_T + \rho \nu_{\mathbf{k}}} \approx \frac{m^2 k_B T V}{w_0} \frac{1}{1 + (l/\xi)^2 k^2 + l^{-2} (l/\xi)^2 / \{1 + (l/\xi)^2\}}. \quad (3.20)$$

For $kl \ll 1$,

$$\langle |\rho_{\mathbf{k}}|^2 \rangle \approx \frac{m^2 k_B T V}{w_0 l^2} \frac{1}{k^2 + \xi^{-2}}. \quad (3.21)$$

Also it can be shown that

$$\xi = l / \sqrt{|\epsilon|}, \quad (3.22)$$

where $\epsilon = T/T_c - 1$, the reduced temperature distance from the critical point.

b. Binary solutions

The linearized Fourier transformed hydrodynamic equations that correspond to (3.6) are

$$\frac{\partial \rho_{\mathbf{k}}}{\partial t} - i\mathbf{k} \cdot \rho \mathbf{v}_{\mathbf{k}} = 0, \tag{3.23a}$$

$$\frac{\partial c_{\mathbf{k}}}{\partial t} + \frac{k^2}{\rho} \left\{ \alpha_h \left(\frac{\partial \mu_h}{\partial c} \right)_{T, c} c_{\mathbf{k}} + \left[\alpha_h \left(\frac{\partial \mu_h}{\partial T} \right)_c + \beta_h \right] T_{\mathbf{k}} \right\} = 0, \tag{3.23b}$$

$$\begin{aligned} \frac{\partial \mathbf{v}_{\mathbf{k}}}{\partial t} - \frac{i\mathbf{k}}{\rho} \left\{ \left[\left(\frac{\partial p_h}{\partial \rho} \right)_T - \frac{\rho}{m^2} x_{\mathbf{k}} \right] \rho_{\mathbf{k}} + \left(\frac{\partial p_h}{\partial T} \right)_\rho T_{\mathbf{k}} \right\} \\ + \frac{\rho}{m^2} i\mathbf{k} y_{\mathbf{k}} c_{\mathbf{k}} + \frac{\eta_h k^2 \mathbf{v}_{\mathbf{k}}}{\rho} + \frac{1}{\rho} \left(\zeta_h + \frac{1}{3} \eta_h \right) \mathbf{k} (\mathbf{k} \cdot \mathbf{v}_{\mathbf{k}}) = 0, \end{aligned} \tag{3.23c}$$

$$\begin{aligned} \rho T \left[\left(\frac{\partial S_h}{\partial T} \right)_{c, \rho} \frac{\partial T_{\mathbf{k}}}{\partial t} + \left(\frac{\partial S_h}{\partial \rho} \right)_{c, T} \frac{\partial \rho_{\mathbf{k}}}{\partial t} + \left(\frac{\partial S_h}{\partial c} \right)_{\rho, T} \frac{\partial c_{\mathbf{k}}}{\partial t} \right] \\ + \left[\lambda_h + \frac{\beta_h^2 T}{\alpha_h} + \beta_h T \left(\frac{\partial \mu_h}{\partial T} \right)_c \right] k^2 T_{\mathbf{k}} + k^2 \beta_h T \left(\frac{\partial \mu_h}{\partial c} \right)_T c_{\mathbf{k}} = 0, \end{aligned} \tag{3.23d}$$

where

$$x_{\mathbf{k}} \equiv 2c\omega_{\mathbf{k}}^{AB} + (1-2c)\omega_{\mathbf{k}}^{BB} + 2c^2\omega_{\mathbf{k}}, \tag{3.24a}$$

$$y_{\mathbf{k}} \equiv \omega_{\mathbf{k}}^{BA} - \omega_{\mathbf{k}}^{BB} + 2c\omega_{\mathbf{k}}, \tag{3.24b}$$

and have omitted subscripts 0.

Using (2.15) and (2.16) we can eliminate the subscripts h from p_h and S_h , but *not* from μ_h in (3.23): $S_h = S$ and

$$\left. \begin{aligned} \left(\frac{\partial p}{\partial \rho} \right)_{T, c} &= \left(\frac{\partial p_h}{\partial \rho} \right)_T - \frac{\rho}{m^2} x_0, \\ \left(\frac{\partial p}{\partial c} \right)_{T, \rho} &= -\frac{\rho^2}{m^2} y_0, \\ \left(\frac{\partial p}{\partial T} \right)_{c, \rho} &= \left(\frac{\partial p_h}{\partial T} \right)_\rho. \end{aligned} \right\} \tag{3.25}$$

Thus in (3.23d) we may replace S_h by S and (3.23c) is rewritten as

$$\begin{aligned} \frac{\partial \mathbf{v}_{\mathbf{k}}}{\partial t} - \frac{i\mathbf{k}}{\rho} \left\{ \left[\left(\frac{\partial p}{\partial \rho} \right)_{T, c} + \frac{\rho}{m^2} x_{0, \mathbf{k}} \right] \rho_{\mathbf{k}} + \left(\frac{\partial p}{\partial T} \right)_\rho T_{\mathbf{k}} + \left[\left(\frac{\partial p}{\partial c} \right)_{T, \rho} + \frac{\rho^2}{m^2} y_{0, \mathbf{k}} \right] c_{\mathbf{k}} \right\} \\ + \frac{\eta_h k^2 \mathbf{v}_{\mathbf{k}}}{\rho} + \frac{1}{\rho} \left(\zeta_h + \frac{1}{3} \eta_h \right) \mathbf{k} (\mathbf{k} \cdot \mathbf{v}_{\mathbf{k}}) = 0, \end{aligned} \tag{3.23c'}$$

where

$$x_{0, \mathbf{k}} \equiv x_0 - x_{\mathbf{k}}, \quad y_{0, \mathbf{k}} \equiv y_0 - y_{\mathbf{k}}. \tag{3.26}$$

Laplace transforming of (3.23) leads to a set of equations that correspond to (3.10), but it is far more complicated and the full expression will not be given here. First $\hat{v}_{\mathbf{k}}^T(s)$ is the same as (3.10d):

$$\hat{v}_{\mathbf{k}}^T(s) = \frac{v_{\mathbf{k}}^T(0)}{s + (\eta_{\mathbf{k}}/\rho)k^2}, \quad (3.27a)$$

and for $T_{\mathbf{k}}(0) = v_{\mathbf{k}}^L(0) = \rho_{\mathbf{k}}(0) = 0$, we obtain

$$\begin{aligned} \hat{c}_{\mathbf{k}}(s) = & \frac{1}{E(\mathbf{k}, s)} \left[s^2 + k^2 \left(s\theta + \left(\frac{\partial p}{\partial \rho} \right)_{T,c} + \frac{\rho}{m^2} x_{0,\mathbf{k}} \right) \right] \\ & \times \left\{ s + \frac{k^2}{\rho C_V} \left[\lambda_h + T \left(\alpha_h \left(\frac{\partial \mu_h}{\partial T} \right)_{\rho,T} + \beta_h \right) \left(\beta_h - \left(\frac{\partial S}{\partial c} \right)_{\rho,T} \right) \right] \right. \\ & \left. + ik \frac{T}{\rho C_V} \left(\frac{\partial S}{\partial \rho} \right)_{T,c} \left(\frac{\partial p}{\partial T} \right)_{\rho,c} \right\} c_{\mathbf{k}}(0) \end{aligned} \quad (3.27b)$$

with θ defined by (3.10f) and

$$\begin{aligned} E(\mathbf{k}, s) = & \left\{ s^2 + k^2 \left[s\theta + \left(\frac{\partial p}{\partial \rho} \right)_{T,c} + \frac{\rho}{m^2} x_{0,\mathbf{k}} \right] \right\} \left\{ s^2 + \frac{k^2 s}{\rho C_V} \left[\lambda_h + T \left(\alpha_h \left(\frac{\partial \mu_h}{\partial T} \right)_{\rho,c} + \beta_h \right) \right. \right. \\ & \left. \left. \times \left(\beta_h - \left(\frac{\partial S}{\partial c} \right)_{\rho,T} \right) \right] + \frac{\alpha_h}{\rho} \left(\frac{\partial \mu_h}{\partial c} \right)_{\rho,T} k^2 s + \frac{\alpha_h \lambda_h}{\rho^2 C_V} \left(\frac{\partial \mu_h}{\partial c} \right)_{\rho,T} k^4 \right\} \\ & + \frac{T}{\rho C_V} \left(\frac{\partial S}{\partial \rho} \right)_{T,c} \left[\left(\frac{\partial p}{\partial c} \right)_{\rho,T} + \frac{\rho^2}{m^2} y_{0,\mathbf{k}} \right] \left(\alpha_h \left(\frac{\partial \mu_h}{\partial T} \right)_{\rho,c} + \beta_h \right) k^4 s \\ & - \frac{T}{C_V} \left(\frac{\partial S}{\partial \rho} \right)_{c,T} \left(\frac{\partial p}{\partial T} \right)_{c,\rho} \left(s + k^2 \frac{\alpha_h}{\rho} \left(\frac{\partial \mu_h}{\partial c} \right)_{\rho,T} \right) k^2 s. \end{aligned} \quad (3.28)$$

The equation $E(\mathbf{k}, s) = 0$ gives four roots for s of the form,

$$s_{\mathbf{k}}^{\pm} = \pm i u_{\mathbf{k}} k - g_{\mathbf{k}} k^2, \quad (3.29a)$$

$$s_{\mathbf{k}}^0 = -f_{\mathbf{k}}^0 k^2, \quad (3.29b)$$

$$s_{\mathbf{k}}^1 = -f_{\mathbf{k}}^1 k^2. \quad (3.29c)$$

$s_{\mathbf{k}}^{\pm}$ corresponds to sound wave modes, and $s_{\mathbf{k}}^0$ and $s_{\mathbf{k}}^1$ correspond to coupled heat transport and diffusion modes. The \mathbf{k} -dependences in $u_{\mathbf{k}}$, $g_{\mathbf{k}}$, $f_{\mathbf{k}}^0$ and $f_{\mathbf{k}}^1$ come from $x_{0,\mathbf{k}}$ and $y_{0,\mathbf{k}}$. Now, since we can write $E(\mathbf{k}, s) = (s - s_{\mathbf{k}}^+) (s - s_{\mathbf{k}}^-) \times (s - s_{\mathbf{k}}^0) (s - s_{\mathbf{k}}^1)$, comparison of this expression with (3.28) yields

$$u_{\mathbf{k}}^2 = \left(\frac{\partial p}{\partial \rho} \right)_{s,c} + \frac{\rho}{m^2} x_{0,\mathbf{k}}, \quad (3.30)$$

$$\begin{aligned} g_{\mathbf{k}} = & \frac{\theta}{2} + \frac{1}{2\rho u_{\mathbf{k}}^2} \left\{ \left[\lambda_h + T \left(\alpha_h \left(\frac{\partial \mu_h}{\partial T} \right)_{c,\rho} + \beta_h \right) \left(\beta_h - \left(\frac{\partial S}{\partial c} \right)_{\rho,T} \right) \right] \right. \\ & \left. \times \left(\frac{1}{C_V} - \frac{1}{C_p} \right) \left(\frac{\partial p}{\partial \rho} \right)_{s,c} - \frac{T}{C_V} \left(\frac{\partial S}{\partial c} \right)_{\rho,T} \left(\left(\frac{\partial p}{\partial c} \right)_{\rho,T} + \frac{\rho^2}{m^2} y_{0,\mathbf{k}} \right) \right\} \end{aligned} \quad (3.31)$$

and

$$u_{\mathbf{k}}^2 f_{\mathbf{k}}^0 f_{\mathbf{k}}^1 = \frac{\alpha_h \lambda_h}{\rho^2 C_V} \left(\frac{\partial \mu_h}{\partial c} \right)_{\rho,T} \left[\left(\frac{\partial p}{\partial \rho} \right)_{T,c} + \frac{\rho}{m^2} x_{0,\mathbf{k}} \right], \quad (3.32)$$

where C_V and C_p are the specific heats at constant volume and pressure, respectively.

Let us now locate the critical solution point. Using (2.13), (2.14) and (2.15) we find

$$\begin{aligned}
 (\partial\mu/\partial c)_{p,T} &= (\partial\mu/\partial c)_{p,T} - (\partial\mu/\partial p)_{c,T}(\partial p/\partial c)_{p,T} \\
 &= \frac{k_B T}{m} \frac{1}{c(1-c)} - \frac{2\rho}{m^2} \left(w_0 - \frac{y_0^2}{2x_0} \right). \tag{3.33}
 \end{aligned}$$

The critical solution point is given by setting $(\partial\mu/\partial c)_{p,T} = 0$, which is the same as that of Deutch and Zwanzig⁶⁾ except for the presence of the extra term involving y_0^2 which arises from the difference between $(\partial\mu/\partial c)_{p,T}$ and $(\partial\mu/\partial c)_{p,T}$, and is of the second order in the differences of the potentials w^{AA} , w^{BB} and w^{AB} .

If we exclude the improbable possibility of f_k^0 and f_k^1 becoming infinite, it is thus seen that u_k , g_k , f_k^0 and f_k^1 all remain finite at the critical solution point in the van der Waals limit. In contrast to the case of one-component fluids, the critical concentration fluctuations do not affect hydrodynamic equations in the van der Waals limit.

The correlation of local concentration fluctuations is obtained by generalizing the relation

$$\begin{aligned}
 \langle \Delta c^2 \rangle &= \frac{V^2 k_B T}{Nm} \frac{1}{(\partial\mu/\partial c)_{p,T}} = \frac{Vm}{\rho} \left\{ \frac{1}{c(1-c)} - \frac{2\rho}{mk_B T} \left(w_0 - \frac{y_0^2}{2x_0} \right) \right\}^{-1} \tag{3.34} \\
 (\Delta c) &\equiv \int [c(\mathbf{r}) - \langle c(\mathbf{r}) \rangle] d\mathbf{r}
 \end{aligned}$$

in the form

$$\langle |c_k|^2 \rangle = \frac{Vm}{\rho} \left\{ \frac{1}{c(1-c)} - \frac{2\rho}{k_B T m} \left(w_k - \frac{y_k^2}{2x_k} \right) \right\}. \tag{3.35}$$

If we omit the term y_k^2 for simplicity, this reduces to that of Deutch and Zwanzig,⁶⁾

$$\langle |c_k|^2 \rangle = \frac{Vm}{\rho} \left\{ \frac{1}{c(1-c)} - \frac{2\rho w_k}{k_B T m} \right\}. \tag{3.35'}$$

If we take (2.3) for $w(\mathbf{r})$, this further reduces for $k \ll l^{-1}$ to

$$\langle |c_k|^2 \rangle \simeq \frac{Vk_B T}{2w_0 l^2} \left(\frac{m}{\rho} \right)^2 \frac{1}{k^2 + \xi^{-2}}, \tag{3.36}$$

where the correlation range of critical fluctuations ξ is

$$\xi = l / \sqrt{|\epsilon|} \tag{3.37}$$

with

$$\epsilon = T/T_c - 1, \tag{3.38}$$

$$T_c = 2\rho w_0 c(1-c) / k_B m. \text{ (critical solution temperature)} \tag{3.39}$$

§ 4. Anomalous transport coefficients

Here we are concerned with transport phenomena occurring over distances sufficiently large compared with l and ξ , and over time interval which is sufficiently long compared with $l/\sqrt{k_B T/m}$ and the characteristic times of critical fluctuations. Such transport phenomena can be described by local hydrodynamic equations which are obtained by averaging semi-macroscopic non-local hydrodynamic equations (2.1) and (2.8) over macroscopically large space-time regions we are concerned with. Equivalently, the transport coefficients entering the local hydrodynamic equation can be obtained from the correlation function expressions for them of the form $\int_0^\infty \langle I(0)I(t) \rangle dt$. The flux I then consists of a part I_L that involves long-range attractive potential and a remaining part I_S that does not. Contributions to the transport coefficient that involve I_S are determined by the dynamics that occur over distances of order σ and persist for the time intervals of order $\sigma/\sqrt{k_B T/m}$, and are not affected by long-range attraction for very large ratios of l/σ . Hence here we are only concerned with the contributions from I_L . I_L can be expressed in terms of local density variables that enter semi-macroscopic hydrodynamic equations (2.1) and (2.8). The time evolution of these density variables can then be described by the semi-macroscopic hydrodynamics. In this respect our calculation has much similarity to earlier phenomenological calculations.^{1),6),9)} However, we consider the long range attraction explicitly also in the time evolution of fluxes. For large l , fluctuations are small decreasing, say, as some inverse powers of l .

Here we are considering leading contributions to anomalous transport coefficients for large l , which are also expressed as some mean square fluctuations. For this purpose we may use semi-macroscopic hydrodynamic equations in the van der Waals limit of § 3 to study the time evolution of fluxes.

a. One-component fluids

i) Shear viscosity

Anomalous part of the shear viscosity is⁹⁾

$$\eta_a = \frac{1}{k_B T V} \int_0^\infty dt \langle J_L^{xy}(t) J_L^{xy}(0) \rangle \quad (4.1)$$

with

$$J_L^{xy} \equiv \frac{1}{2V} \sum_{\mathbf{k}} \frac{1}{m^2} \frac{\partial \omega_{\mathbf{k}}}{\partial k_x} k_y (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle). \quad (4.2)$$

For the time evolution of J_L^{xy} , we here use the linearized hydrodynamic equations of § 3. Non-linear corrections, which cannot be ignored *a priori* even in the van der Waals limit, will be estimated later in § 5. Since (4.2) contains only the mass density, we set $v_{\mathbf{k}}^L(0) = T_{\mathbf{k}}(0) = 0$ in (3.10a), where we assume

that equal-time correlations of $\rho_{\mathbf{k}}$ with $\mathbf{v}_{\mathbf{k}}$ and $T_{\mathbf{k}}$ are not so important as to affect the result seriously. Then, for small k we can show that^{*}

$$\hat{\rho}_{\mathbf{k}}(s)/\rho_{\mathbf{k}}(0) \cong \left(1 - \frac{1}{\gamma_{\mathbf{k}}}\right) \frac{1}{s - s_{\mathbf{k}}^0} + \frac{1}{2\gamma_{\mathbf{k}}} \left(\frac{1}{s - s_{\mathbf{k}}^+} + \frac{1}{s - s_{\mathbf{k}}^-} \right). \quad (4.3)$$

That is,

$$\rho_{\mathbf{k}}(t) = \left\{ \left(1 - \frac{1}{\gamma_{\mathbf{k}}}\right) \exp(-ts_{\mathbf{k}}^0) + \frac{1}{2\gamma_{\mathbf{k}}} (\exp(-ts_{\mathbf{k}}^+) + \exp(-ts_{\mathbf{k}}^-)) \right\} \rho_{\mathbf{k}}(0). \quad (4.4)$$

According to (3.17) and (3.18), $\gamma_{\mathbf{k}} \gg 1$ for sufficiently large l as well as near the critical point, and only the first term of (4.4) is important. After substituting $\rho_{\mathbf{k}}(t)$ into $J_L^{xy}(t)$, we find (4.1) that involves equal-time correlation of four ρ 's, which can be replaced by the product of two $\langle |\rho_{\mathbf{k}}|^2 \rangle$ if we ignore higher order contributions in l^{-1} . Thus, with the use of (3.15b), (3.17) and (3.20), we obtain

$$\eta_a = \frac{3}{2^6 \pi^2} \frac{C_V k_B T m^2 u_0^2}{\omega_0 \lambda_h} \frac{1}{l} \frac{1}{1 + (l/\xi)^2} \int_0^\infty dx x^4 \frac{\{1 + (\rho \omega_0 / m^2 u_0^2)\} x^2 + 1}{[x^2 + (l/\xi)^2 / \{1 + (l/\xi)^2\}]^3}. \quad (4.5)$$

Near the critical point where $l \ll \xi$ but the mean field theory is still valid, this reduces to

$$\eta_a = \frac{3}{2^7 \times 5 \pi^2} \frac{C_V k_B T m^2 u_0^2}{\omega_0 \lambda_h} \frac{1}{l} \frac{1}{\sqrt{|\epsilon|}}, \quad (4.6)$$

where (3.22) has been used. The same temperature dependence has been predicted by Fixman for real fluids.⁹⁾ However, he estimates the magnitude of this anomalous term to be very small for CO₂. Mountain and Zwanzig⁶⁾ obtained η_a which stays finite at $\epsilon = 0$. The difference arises from the fact that in our treatment $\gamma_{\mathbf{k}=0}$ diverges as $1/|\epsilon|$ in the van der Waals limit.

ii) *Bulk viscosity*

Anomalous part of the bulk viscosity ζ_a now becomes⁶⁾

$$\zeta_a = \frac{1}{k_B T V} \int_0^\infty dt \langle J_L^v(t) J_L^v(0) \rangle \quad (4.7)$$

with

$$J_L^v = \frac{1}{6V} \sum_{\mathbf{k}} \frac{1}{m^2} \left(3\omega_{\mathbf{k}} + \mathbf{k} \cdot \frac{\partial}{\partial \mathbf{k}} \omega_{\mathbf{k}} \right) (\rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle). \quad (4.8)$$

A calculation which is quite similar to that for η_a leads to

^{*}) This can be done very easily by first setting $\hat{\rho}_{\mathbf{k}}(s)/\rho_{\mathbf{k}}(0) \cong A_0/(s - s_{\mathbf{k}}^0) + A_+/(s - s_{\mathbf{k}}^+) + A_-/(s - s_{\mathbf{k}}^-)$ and determining A 's by $A_\alpha = \lim_{s \rightarrow s_{\mathbf{k}}^\alpha} \{(s - s_{\mathbf{k}}^\alpha) \hat{\rho}_{\mathbf{k}}(s)/\rho_{\mathbf{k}}(0)\}$, ($\alpha = 0, +, -$).

$$\zeta_a = \frac{1}{4\pi^2} \frac{C_V k_B T m^2 u_0^2}{\omega_0 \lambda_h} \frac{1}{l} \frac{1}{1 + (l/\xi)^2} \int_0^\infty dx \frac{[1 + (1 + \rho\omega_0/m^2 u_0) x^2]^2 (1 + x^2/3)^2}{[x^2 + (l/\xi)^2 / \{1 + (l/\xi)^2\}]^3}. \quad (4.9)$$

This reduces, for $\xi \gg l$, to

$$\zeta_a = \frac{3}{2^6 \pi} \frac{C_V k_B T m^2 u_0^2}{\omega_0 \lambda_h} \frac{1}{l} \frac{1}{|\epsilon|^{5/2}}. \quad (4.10)$$

The anomaly obtained is stronger than those of Mountain and Zwanzig⁶⁾ and of de Sobrino.⁸⁾

iii) Thermal conductivity

Anomalous part of the thermal conductivity λ_a is now written as⁶⁾

$$\lambda_a = \frac{1}{3V k_B T^2} \int_0^\infty dt \langle \mathbf{Q}_L(t) \cdot \mathbf{Q}_L(0) \rangle, \quad (4.11)$$

$$\mathbf{Q}_L \equiv -\frac{1}{2V} \sum_{\mathbf{k}} \frac{1}{m^2} \left[2\omega_{\mathbf{k}} \mathbf{j}_{-\mathbf{k}} + \mathbf{k} \cdot \mathbf{j}_{-\mathbf{k}} \frac{\partial \omega_{\mathbf{k}}}{\partial \mathbf{k}} \right] \rho_{\mathbf{k}}, \quad (4.12)$$

where $\mathbf{j}_{\mathbf{k}}$ is the Fourier component of mass current density. $\mathbf{Q}_L(t)$ is obtained by using linearized semi-macroscopic hydrodynamic equations of § 3. Then, only the transverse component of $\mathbf{j}_{\mathbf{k}}$ contributes to (4.11)⁶⁾ and we find

$$\lambda_a = \frac{\rho^2 \omega_0 k_B}{3\pi^2 m^2} \frac{1}{l} \frac{1}{1 + (l/\xi)^2} \int_0^\infty dx \frac{1}{1 + x^2} \frac{1}{x^2 + (l/\xi)^2 / \{1 + (l/\xi)^2\}} \\ \times \frac{1}{\eta_h + (\lambda_h \omega_0 \rho / C_V m^2 u_0^2) (l/\xi)^2 (1 + [1 + (\xi/l)^2 x^2]) / (1 + [1 + (\rho\omega_0/m^2 u_0^2)] x^2)}. \quad (4.13)$$

Near the critical point $\xi \gg l$, this reduces to

$$\lambda_a \approx \frac{\rho^2 \omega_0 k_B}{6\pi m^2 \eta_h} \frac{1}{l} \frac{1}{\sqrt{|\epsilon|}}. \quad (4.14)$$

The temperature dependence agrees with that of Fixman's result.⁹⁾

b. Binary solution

i) Diffusion constant

The diffusion constant D is expressed in the well-known way:

$$D = \frac{1}{\rho^2 \langle \Delta c^2 \rangle} \int_0^\infty \langle I^x(t) I^x(0) \rangle dt \quad (4.15)$$

with

$$I^x \equiv \int i^x(\mathbf{r}) d\mathbf{r}. \quad (4.16)$$

In order to express I^x in terms of hydrodynamic variables of §§ 2 and 3, let us express a quantity

$$\frac{1}{V} \sum'_{\mathbf{k}} v_{\mathbf{k}}^x c_{-\mathbf{k}}$$

in molecular variables where \sum' is the sum over \mathbf{k} that satisfy $|\mathbf{k}| < k_0$, k_0 being determined below. By the definitions of \mathbf{v} and c , we have

$$\left. \begin{aligned} v_{\mathbf{k}} &= \sum_j v_j \exp(i\mathbf{k} \cdot \mathbf{r}_j), \\ c_{\mathbf{k}} &= \frac{m}{\rho} \sum_j [(1-c)f_j^A - cf_j^B] \exp(i\mathbf{k} \cdot \mathbf{r}_j), \end{aligned} \right\} \quad (4.17)$$

where $f_j^A = 1$ or 0 according to the species of j is A or B , respectively, and similarly for f_j^B . Then it is easy to show that

$$\frac{1}{V} \sum'_{\mathbf{k}} v_{\mathbf{k}}^x c_{-\mathbf{k}} = \frac{m}{\rho} \sum_{j,l} v_j^x [(1-c)f_l^A - cf_l^B] \Delta(\mathbf{r}_j - \mathbf{r}_l), \quad (4.18)$$

where

$$\Delta(\mathbf{r}) \equiv \frac{1}{V} \sum'_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}).$$

We now choose k_0 sufficiently large so that $\Delta(\mathbf{r})$ vanishes whenever r exceeds the hard sphere radius.*) Thus only the terms $j=l$ remain in (4.18) and we obtain

$$\begin{aligned} (4.18) &= \Delta(0) \frac{m}{\rho} \sum_j v_j^x [(1-c)f_j^A - cf_j^B] \\ &= \frac{\Delta(0)}{\rho} m \left\{ (1-c) \sum_{j \in A} v_j^x - c \sum_{j \in B} v_j^x \right\}. \end{aligned} \quad (4.19)$$

This quantity equals, on the average, $(\Delta(0)/\rho) m N c (1-c) [v_A^x - v_B^x]$. Thus by comparison with (2.9d), we find on the average

$$I^x = \frac{\rho}{\Delta(0)} \frac{1}{V} \sum'_{\mathbf{k}} v_{\mathbf{k}}^x c_{-\mathbf{k}}. \quad (4.20)$$

The main contribution to D then arises from small k in (4.20) and the subsequent calculation proceeds in the same way as before. $v_{\mathbf{k}}^x$ is divided into the transverse and longitudinal components $v_{\mathbf{k}}^{Tx}$ and $v_{\mathbf{k}}^{Lx}$, respectively. $v_{\mathbf{k}}^{Lx}$ consists of a part that obeys heat transport equation and another part that obeys sound wave equation. The former part and $v_{\mathbf{k}}^{Tx}$ that obeys the Navier-Stokes equation give main contributions to D . Thus, apart from a finite multiplicative

*) Alternatively, and in a more general way, instead of having $\sum'_{\mathbf{k}}$ we may insert an appropriate form factor $g(k)$ which satisfies the properties required here and $g(0) \neq 0$ without changing the final result.

factor we may consider only the contribution arising from $v_k^{T_x}$. In this way we find near the critical solution point,

$$\begin{aligned} L &\equiv \frac{1}{V} \int_0^\infty \langle I^x(t) I^x(0) \rangle dt = \text{const} \times \frac{1}{V} \int d\mathbf{k} \frac{\langle |c_k|^2 \rangle}{\{(\eta_h/\rho) + D_h\} k^2} \\ &= \text{const} \times \frac{\xi}{l^2} = \text{const} \times \frac{1}{l} \frac{1}{\sqrt{|\epsilon|}}, \end{aligned} \quad (4.21)$$

where (3.36) has been used, and const does not contain l and ϵ .

Since by (3.34) $\rho^2 \langle \Delta c^2 \rangle / V = \text{const} \times |\epsilon|^{-1}$, we find

$$D = \text{const} \times \frac{\sqrt{|\epsilon|}}{l}. \quad (4.22)$$

The processes that contribute to D is the same as those considered by Swift.³⁾ However, here η_h and D_h are known to contain no anomaly at T_c . Comparing (4.14) and (4.21) the concentration conductivity L and the thermal conductivity behave in the same way as $l^{-1}|\epsilon|^{-1/2}$, which is precisely what Swift assumed and is in agreement with recent experiments,¹²⁾ although the value of the exponent of ϵ itself is different.

ii) Shear viscosity

The calculation of shear viscosity is rather similar to that for one-component fluids, where instead of ρ_k we have c_k which obeys the diffusion equation with the finite diffusion constant D_h , and we have

$$\eta_a = \text{const} \times \xi^{-1} = \text{const} \times \frac{1}{l} \sqrt{|\epsilon|}. \quad (4.23)^*)$$

The different temperature dependence is due to the fact that D_h which corresponds to $\lambda_h/\rho C_p \sim |\epsilon|$ remains finite at T_c . Thus the shear viscosity remains finite at T_c for this model in the approximation studied.

iii) Bulk viscosity

The calculation of bulk viscosity also parallels that for one-component fluids and the result is

$$\zeta_a = \text{const} \times \xi^{-1} (\xi/l)^4 = \text{const} \times \frac{1}{l} |\epsilon|^{-3/2} \quad (4.24)$$

which is less singular than that of Deutch and Zwanzig.⁶⁾

iv) Thermal conductivity

The anomalous part λ_a can be expressed as

*) Full expression for η contains a term which remains finite at T_c . This is in contrast to D , (4.22), which actually vanishes at T_c .

$$\lambda_a = \frac{1}{3Vk_B T^2} \int_0^\infty dt \langle \mathbf{Q}_L(t) \cdot \mathbf{Q}_L(0) \rangle, \quad (4.25)$$

where \mathbf{Q}_L is the part of heat flux that contains long-range attractive potential, and, if we ignore the total density fluctuation, is written as

$$\mathbf{Q}_L = -\frac{\rho}{2V} \sum_{\mathbf{k}} (\mathbf{Y}_0 + \mathbf{Y}_{\mathbf{k}}) \cdot \mathbf{j}_{-\mathbf{k}} c_{\mathbf{k}} - \frac{\rho}{V} \sum_{\mathbf{k}} \mathbf{W}_{\mathbf{k}} \cdot \mathbf{i}_{-\mathbf{k}} c_{\mathbf{k}}, \quad (4.26)$$

where \mathbf{Y} and \mathbf{W} are the second rank tensors defined by

$$\mathbf{Y}_{\mathbf{k}} \equiv y_{\mathbf{k}} \mathbf{1} + \mathbf{k} \frac{\partial y_{\mathbf{k}}}{\partial \mathbf{k}} \quad \text{and} \quad \mathbf{W}_{\mathbf{k}} \equiv w_{\mathbf{k}} \mathbf{1} + \mathbf{k} \frac{\partial w_{\mathbf{k}}}{\partial \mathbf{k}} \quad (4.27)$$

with $\mathbf{1}$ the unit dyadic, and $y_{\mathbf{k}}$ and $w_{\mathbf{k}}$ are given by (3.24b) and the Fourier transform of (2.9e), respectively.

The subsequent calculation is the same as before where $\mathbf{i}_{-\mathbf{k}}$ can be expressed in terms of $c_{\mathbf{k}'}$ and $\mathbf{v}_{\mathbf{k}'}$ as in (4.20), and we find that

$$\lambda_a = \text{const} \times \xi/l^2 = \text{const} \times \frac{1}{l} \frac{1}{\sqrt{|\epsilon|}}. \quad (4.28)$$

v) *Thermal diffusion constant*

Anomalous part of thermal diffusion constant D_a^T is expressed as

$$D_a^T = \frac{1}{3k_B T V} \int_0^\infty dt \langle \mathbf{I}(t) \cdot \mathbf{Q}_L(0) \rangle, \quad (4.29)$$

where \mathbf{I} and \mathbf{Q}_L are given by (4.20) and (4.26), respectively, and by the same calculation as before we find

$$D_a^T = \text{const} \times \xi/l^2 = \text{const} \times \frac{1}{l} \frac{1}{\sqrt{|\epsilon|}}. \quad (4.30)$$

§ 5. Discussion

In the preceding sections we have considered the lowest order corrections of critical fluctuations to the transport coefficients when the range of attractive potential is very large. The anomalous parts are of the general form $l^{-1}f(\epsilon)$. This can be readily understood. The lowest order fluctuation corrections to equilibrium quantities are of the general form $l^{-3}g(\epsilon)$.¹³⁾ The time integrals of the correlation function expressions produce factors like $\xi^2 F(\epsilon)$, and thus the fluctuation corrections to transport coefficients are $l^{-3}\xi^2 g(\epsilon) = l^{-1}(\xi/l)^2 g(\epsilon) F(\epsilon) = l^{-1}f(\epsilon)$ because of (3.22) and (3.37). This vanishes as $l \rightarrow \infty$ for fixed ϵ , which is natural if we note that transport coefficients are mean square fluctuations in a sense.

The various anomalous contributions to transport coefficients obtained here

cannot be compared with experiments directly because of the rather special models adopted here.*) In order to discuss asymptotic behaviors in the truly critical regions, the study of higher order terms including nonlinear terms in the semi-macroscopic hydrodynamic equations of § 2 is indispensable, which is a difficult task and will be discussed briefly in the following.

We now estimate the effects of including nonlinear terms in the full hydrodynamic equations of § 2 which are written in the matrix form as

$$\frac{\partial}{\partial t} A_{\mathbf{k}} = -M_{\mathbf{k}} \cdot A_{\mathbf{k}} + \sum_{n=2}^{\infty} \sum_{\{\alpha_i\}} \sum_{\{\mathbf{k}_i\}}' C(\mathbf{k} | \{\mathbf{k}_i\}, \{\alpha_i\}) A_{\mathbf{k}_1}^{\alpha_1} A_{\mathbf{k}_2}^{\alpha_2} \cdots A_{\mathbf{k}_n}^{\alpha_n}, \quad (5.1)$$

where $A_{\mathbf{k}}$ is a column matrix composed of Fourier transformed hydrodynamic variables and C is also a column matrix that represents nonlinear coupling among A 's. We write this symbolically as

$$\frac{\partial}{\partial t} A = -MA + \sum_n g_n A^n \text{ or } A(t) = e^{-Mt} \left[A(0) + \sum_n \int_0^t ds e^{Ms} g_n A^n(s) \right]. \quad (5.2)$$

Iteration of this yields $A(t)$ in terms of $A(0)$.

Now, anomalous part of a transport coefficient $\Theta = \text{const} \times \int_0^{\infty} \langle J_1(t) J_2(0) \rangle dt$ has a flux of the general form¹⁴⁾

$$J_i = \frac{1}{V} \sum_{\mathbf{k}} f_{i\mathbf{k}}^{\alpha\beta} A_{\mathbf{k}}^{\alpha} A_{-\mathbf{k}}^{\beta}. \quad (i=1,2) \quad (5.3)$$

In $A_{\mathbf{k}}^{\alpha}(t)$ $A_{-\mathbf{k}}^{\beta}(t)$ we substitute solutions of (5.2) obtained by iteration. We then find that Θ can be written symbolically as

$$\begin{aligned} \Theta = & \text{Sums of terms like } \sum^{2+n_1+n_2+\cdots+n_i+n_1'+n_2'+\cdots+n_j'-i-j} f_1 f_2 \\ & \times \frac{g^{i+j}}{M^{i+j+1}} \langle A^{n_1+n_2+\cdots+n_i+n_1'+n_2'+\cdots+n_j'-i-j+4} \rangle, \end{aligned} \quad (5.4)$$

where n 's ≥ 2 and g and M represent Fourier transforms of elements of M and g 's, and g at least contains a factor k 's and each \sum represents a sum over a wave vector. In order to find an upper bound to the magnitude of (5.4), we take M to be of the order of $(l/\xi)^{\alpha} k^2$ where $\alpha=2$ for one component fluids and $\alpha=0$ for binary solutions, and take A 's to be critical variables such as $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$. For large l , then, the average in (5.4) can be replaced by the sums of products of pair correlations $\langle |A_{\mathbf{k}}|^2 \rangle \sim 1/(l/\xi)^2$ since main contributions to (5.4) arise from k 's $\sim \xi^{-1}$. This produces $1 + (1/2) (\sum n - i - j)$ Kronecker's deltas that restrict sums over wave vectors where $\sum n \equiv n_1 + n_2 + \cdots + n_i + n_1' + n_2' + \cdots + n_j'$. Then, each term in (5.4) becomes, noting $\xi/l = |\epsilon|^{-1/2}$,

*) If there is a system well described by the present model, our results will well represent initial behaviors of l times anomalous transport coefficients as the critical point is approached. Our results correspond to the RPA calculations of specific heat which behave as $l^{-3} |\epsilon|^{-1/2}$ and do not give the correct critical exponent.

$$f_1 f_2 \xi^{-d(2+\Sigma n-i-j)} \xi^{d[1+(1/2)(\Sigma n-i-j)]} \xi^{i+j+2} (\xi/l)^{\Sigma n-i-j+4+(i+j+1)\alpha}$$

$$= f_1 f_2 l^{-d+2} |\epsilon|^{-(3+(\alpha-d)/2)} (l^{d/2-1} |\epsilon|^{1-(d/4+(\alpha/2))-(i+j)}) (|\epsilon|^{d/4-1/2} / l^{d/2})^{\Sigma(n-2)}, \quad (5.5)$$

where d is the dimensionality of space. From this result we see that the terms with $n_i, n_i' > 2$ can be ignored, and the effects of nonlinear terms are unimportant for $|\epsilon| \gtrsim l^{-(d/2-1)/(1-d/4+\alpha/2)}$. The expansion parameter $l^{-(d/2-1)} |\epsilon|^{-(1-d/4+\alpha/2)}$ for the cases $n_i = n_i' = 2$ is much larger than that for the equilibrium quantities, $l^{-d} |\epsilon|^{-1/2}$, for $d=3$.¹³⁾ However, it is quite possible that we have grossly overestimated the non-linear effects, and the actual expansion parameter can be much smaller.

The errors introduced by using the pair approximation for $\langle A^n \rangle$ and for using classical values of critical exponents can be estimated as in equilibrium properties,¹³⁾ and are characterized by the equilibrium expansion parameter mentioned above, and we thus see that all the correction terms to the results of the preceding sections vanish much faster as $l \rightarrow \infty$ with fixed ϵ .

In the present paper we have considered the lowest order corrections to transport coefficients due to critical fluctuations when l is large, but our model itself is not limited to the lowest order corrections, and it is hoped that the model will be useful in the study of transport properties in the truly critical regions also.

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